Networked computing for ab initio modeling the chemical storage of alternative energy: Fourth term report (June-August 2016)

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Abstract

A vibrational analysis for the OH + H$_2$ → H$_2$O + H process has been performed for investigating both the effect of the initial vibrational level of reactants on the system's reactive probability and the disposal of energy into the vibrational degrees of freedom of the molecules after non reactive collisions. In the first case different results have been obtained from the vibrational excitation of H$_2$ and OH: While OH vibrational excitation has no appreciable effect on system's reactive probability the opposite happens for the case of H$_2$. Regarding vibrational excitation of the colliding molecules, our calculations have shown that non reactive events are entirely vibrationally adiabatic for H$_2$ and partially non adiabatic for OH.

On the technological innovation transfer side of our computational interests, partial progress has also been made in reactivating the PROGEO apparatus after its transfer from Acerra.

The evolution of these two components of our ESR project has been reported at the 1st annual workshop of the ITN-EJD-TCCM PhD program and will be the object of two meetings to be held at the Perugia University: the first one to be held at the Department of Chemistry, Biology and Biotechnologies by the mid of October as a formal closure of

the stage with PLC SYSTEM; the second one to be held at the Department of Civil and Environmental Engineering as the starting event of the new ESODIS project.

Report

1) OH + H$_2$ → H$_2$O + H reactivity enhancement by vibrational excitation of reactants.

The experimental and theoretical foundations of our study of the OH + H$_2$ → H$_2$O + H process were discussed in the previous report[1] by first introducing the quantum-classical (QC) method[2] and then reporting a comparative analysis of the QC results with the ones obtained in a full quantum (QQ) calculation of Chen *et al* [3]. The method proved to be reliable and accurate for the considered process and this prompted further calculations. Next we calculated the effect of the vibrational excitation of reactants in enhancing the reactivity of the process at different values of translational energy. As shown in the Table 1, the reactive probability of the investigated process is greatly enhanced when the H$_2$ reactant molecule is vibrationally excited to *v*=1 and *v*=2. From the Table 1, one can also argue that this behaviour is further increased when the excitation is done to the *v*=2 state. No change in system's reactive probability is observed when the OH vibrational state is excited to the *v*=1 or *v*=2 states. This behaviour (also observed in other works[4]) could suggest a mechanism composed by a break of the H$_2$ bond and the capture of one of the H atoms by the OH reactant. Nevertheless, a more detailed analysis is needed in order to state a clear mechanism.

Translational	Reactive Probability				
Energy / eV	$v_{OH}=0; v_{H2}=0$	$v_{OH}=0; v_{H2}=1$	$v_{OH}=0; v_{H2}=2$	$v_{OH}=1; v_{H2}=0$	$v_{OH}=2; v_{H2}=0$
0.2	0.008	0.214	0.465	0.008	0.009
0.3	0.141	0.422	0.591	0.145	0.144
0.4	0.324	0.538	0.672	0.322	0.319
0.5	0.431	0.617	0.732	0.433	0.427

Table. 1 State specific (J=L=0, $j_{OH}=j_{H2}=0$) H_2 + OH → H_2O + H, QC reactive probability at different values of the translational energy and reactants' vibrational levels.

We have also carried out a state to state vibrational analysis of the OH + H_2 process at different translational energies for the non reacted part of the system wavefunction to see if the collision produces an exchange of energy among different degrees of freedom (like the transfer of energy from the translational degree of freedom to the vibrational ones. Preliminary calculations show that non reactive probabilities are fully vibrationally adiabatic for H_2 and partially non adiabatic for OH.

2) Progress in reactivating the PROGEO apparatus after its transfer from Acerra

My stage activities with the PLC SYSTEM during the months June-August have been devoted to identifying the problems spotted after the transfer of the PROGEO apparatus from Acerra to Perugia with the operators of the PLC SYSTEM, the members of the Departments of Chemistry Biology and Biotechnology and of Civil and Environmental engineering, the personnel of the RD Power srl and the RPC srl. The three sections of the apparatus have been examined in detail. Namely they are:

a) The appropriate handling of renewable energy sources to generate hydrogen.

b) The optimal management of the carbon dioxide reduction to

methane.

c) The storage of the produced methane as methane hydrate.

A problem common to all sections was found to be the lack of documentation of the disconnection phase (and the consequent difficulty of a correct reassembling of the several components like the heat exchanger, automated control circuitry, the temperature monitoring at the various points of the reactor, etc.). This has created (and is still creating) difficulties to the restoring of the original functionalities.

As to the first section the major problem has been the impossibility of using the electrolyser due to the high demand of electricity especially at restarting phase. For carrying out the experiments the electrolyser has been replaced by a hydrogen bottle.

As to the second section the major problem was the reintegration of the heat exchanger (with the consequent reduction of yield) and the difficulty of operating with the gas chromatography in the present installation.

As to the third section no attempt has been already made to establish a physical connection.

Despite all that the apparatus is presently used for refinement of its working parameters and for comparison with the new apparatus ESODIS (0.5 MW), with the newly designed electrolyser and with the new developments of the simulation software.

3) The presentation of the project to the colleagues of the University

On the above illustrated ground two initiatives are being prepared for

illustrating the features of PROGEO and the perspectives of the underlying research project ESODIS.

The Programme of the PROGEO project to be held on October 19 reads:

15:00-15:10. "Institutions, men and enterprises of the Progeo project" (A. Laganà, Department of Chemistry, Biology and Biotechnologies)

15:10-15:35. "Electric networks and renewable energy storage" (F. Sarnataro, PLC System S.r.l.)

15:35-16:00. "Methane production from CO_2 and its storage as Clathrate hydrate" (S. Arca, E. D'Alessandro, RD Power S.r.l.)

16:00. Open discussion of N. Balucani with Chemistry and Chemical Sciences students on professional experiences of the participating chemists with the participation of the ITN-EJD-TCCM PhD student Carles Martí (Barcelona).

The Programme of the Esodis project to be held on November the 11th reads:

9:30-10:00. Welcome from Prof. F. Moriconi (Rector of the University of Perugia), Prof. A. Materazzi (Director of the Department of Civil and Environmental Engineering), Prof. F. Tarantelli (Director of the Department of Chemistry, Biology and Biotechnologies)

10:00-10:20. Prof. A. Pezzini (Counselor and quaestor at CESE (European Economic and Social Committee) Circular economy: job creation for SME).

10:20-10:35. Oenologist M. Ragusa (Researcher on Wine and Oil) The wine sector: sustainable applications of Power to Gas.

10:35-10:50. Dr. A. Damiani (APRE President) APRE for the internationalization of the Italian energetic technologies.

10:50-11:10. Prof. A. Laganà (University of Perugia) Open molecular sciences for the use of renewable energies

11:10-11:30. Dr. A. Capriccioli (ENEA, Frascati) Electrodes and reactors for the synthesis of carbon compounds.

11:30-11:45. Dr. S. Arca (RD Power srl) Gas storage in clathrate hydrates.

11:45-12:00. Prof. S. Falcinelli (University of Perugia) Production of CH_4 from CO_2 without catalyst?

12:00-13:00. Contributions from the floor

13:00-13:30 .Conclusions

13:30. Buffet

4) Attendance to the ITN-EJD-TCCM 1st Annual Workshop at Paris

During the 18th, 19th and 20th of July the 1st Annual Worksop ITN-EJD-TCCM was organized at the Pierre and Marie Curie University in Paris [5]. It has been the first of three workshops in order to make a following of all the 15 PhD projects. The event was organized in two evaluation schemes, a 15 minute slide exposition of the work done to an audience consistent on supervisors who had the opportunity of seeing their students present their work – for some of them this was a first, and a poster session were a personal discussion of the work produced was done with experts on the field.

Finally, Some experienced researchers joined the workshop to evaluate the presentation, discussion and participation skills of the ITN-participants. Every student was evaluated by means of a small questionnaire and challenged to engage in discussions about their work.

REFERENCES

1] C. Martí, Networked computing for *ab initio* modeling the chemical storage of alternative energy: Third term report (March-May 2016).

2] N. Balakrishnan, G. D. Billing, Integral cross sections and rate constants for the reaction $OH + H_2 \rightarrow H_2O + H$: A semiclassical wave packet approach, J. Chem. Phys. 101 (4) (1994) 2785. (1982).

3] J. Chen, X. Xu, X. Xu, D. H. Zhang, A global potential energy surface for the $H_2 + OH \leftrightarrow H_2O + H$ reaction using neural networks, J. Chem. Phys. 138 (22) (2013) 154301.

4] R. Zellner, W. Steinert, Vibrational Rate Enhancement in the Reaction $OH + H_2 \rightarrow H_2O + H$, Chemical Physics Letters 81 (3) (1981) 568-572.

5] https://tccm-alumni.qui.uam.es/?p=1984